The University of Chicago

THE RELATION BETWEEN THE ALPHA-RAY ACTIVITIES AND RANGES OF RADIOACTIVE SUBSTANCES

A DISSERTATION
SUBMITTED TO THE FACULTY
OF THE OGDEN GRADUATE SCHOOL OF SCIENCE
IN CANDIDACY FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY

BY
EDWIN DANIEL LEMAN

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INTRODUCTION

At the present time all previous work tends to indicate that the number of ions, and therefore the ionization current in air due to a single particle of range R, is very closely proportional to the two-thirds power of R.[1] This can be represented by the equation, $I = kR^{\frac{3}{2}}$, where I is the ionization current, R the range, and k a constant for particles of all ranges. McCoy and Viol[2] have shown that the relative α-ray activities in the thorium series, as calculated from this equation, are in good accord with experimental values. The purpose of this paper is to show that the relative activities of radium and its short-lived products and of radioactinium and its subsequent products are also in good agreement with those calculated from the known ranges. Notes on the period and range of radioactinium and the period of actinium X are also included. The subject-matter of this thesis has been published in three papers.[3]

[1] Geiger, *Proc. Roy. Soc.*, A, **82**, 486, 1909; Taylor, *Phil. Mag.*, **21**, 371, 1911; McCoy, *Phys. Rev.*, **1**, 393, 1913.

[2] *Phil. Mag.*, **25**, 333, 1913.

[3] McCoy and Leman, *Phys. Zeit.*, **14**, 1280 (1913); *Phys. Rev.*, **4**, 409 (1914); *ibid.*, **6**, 184 (1915).

CHAPTER I

THE RELATION BETWEEN THE α-RAY ACTIVITIES AND RANGES OF RADIUM AND ITS SHORT-LIVED PRODUCTS

The latest available data on the radium series[1] which are used in this paper are given in Table I.

TABLE I

THE RADIUM SERIES

	Symbols	Period	Rays	Ranges (Cm. at 15° C.)
Radium	Ra	1730 years	α, β	3.30
Emanation	Em	3.85 days	α	4.16
Radium *A*	Ra*A*	3.00 minutes	α	4.75
Radium *B*	Ra*B*	26.7 minutes	β	.....
Radium C_1	RaC_1	19.5 minutes	α(?), β	.....
Radium C_2	RaC_2	1.4 minutes	β	.....
Radium *C'*	Ra*C'*	10^{-6} seconds(?)	α	6.94

The accepted scheme of disintegration in this series, according to Fajans,[2] is as follows:

$$\mathrm{Ra}\xrightarrow[\alpha,\beta]{}\mathrm{Em}\xrightarrow{\alpha}\mathrm{Ra}A\xrightarrow{\alpha}\mathrm{Ra}B\xrightarrow{\beta}\mathrm{Ra}C_1\begin{cases}\xrightarrow{\alpha}\mathrm{Ra}C_2\xrightarrow{\beta}?\\ \xrightarrow[\beta]{}\mathrm{Ra}C'\xrightarrow{\alpha}\mathrm{Ra}D\xrightarrow{\beta}\mathrm{Ra}E\xrightarrow{\beta}\mathrm{Ra}F\xrightarrow{\alpha}\end{cases}$$

According to this view, the product formerly called radium *C* is complex: C_1, which is the product of *B*, disintegrates in two ways: the first (principal) with the production of a β-particle giving *C'*; the second (subordinate) with the expulsion of an α-particle, giving C_2. The product *C'* also gives α-rays, and of every 10,000 α-particles produced by the *C* components all but three are due to the change of *C'* into *D*, the balance being due to the change of C_1 into C_2.[3] If we assume that these conclusions are essentially correct, we see that the effect on the activity caused by a minute fraction of the α-particles of radium *C*, having a different range from those of the main fraction, would be negligibly small. I shall

[1] Kolowrat, *Le Radium*, **11**, 1, 1914.

[2] *Phys. Zeit.*, **13**, 699, 1912.

[3] Fajans, *loc. cit.*

neglect the complexity of *C* in the discussions in this paper, merely pointing out that the present work furnishes no data regarding this important question.

The method of determining the relative α-ray activities of Ra and its short-lived products consisted in preparing a Ra-$BaSO_4$ film free from all of the subsequent products of Ra and measuring its initial and final activities. The activities of such films increased for about six weeks after the preparation of the film and then remained practically constant during several months of observation, the constant activity in each case being taken as the final. The Ra-$BaSO_4$ film, free from its subsequent products, was prepared in the following manner: One c.c. of a solution of pure radium chloride in dilute hydrochloric acid was diluted to 10 c.c.; the solution was heated to its boiling-point, and a current of air was bubbled through it for thirty minutes, the solution being kept near its boiling-point and a few cubic centimeters of water being added from time to time to replace that lost by evaporation. This procedure kept the solution free from emanation, and allowed Ra*A* to decay practically completely. A few drops of lead acetate solution were then added and hydrogen sulphide passed in. The lead sulphide, which was precipitated, removed *B*, *C*, *D*, *E*, and *F*.[1] The precipitate was rapidly filtered off, and a current of air was again bubbled through the filtrate for ten minutes, keeping it near its boiling-point and the volume constant. Lead sulphide was again precipitated in the solution, the precipitate filtered off, and the filtrate again treated in the manner just described, making a total of three precipitations of lead sulphide and removing practically every trace of the products of radium. The various operations to this point had taken about fifty minutes. The filtrate from the last treatment was put into a 15 c.c. centrifuge tube, 1 c.c. of $N/100$ barium chloride solution added, then a few drops of dilute sulphuric acid. The solution was well shaken and then centrifuged. The supernatant solution was decanted from the precipitate, and the latter was well washed, by decantation, with water acidified with a few drops of HCl, and finally with alcohol. A small portion of this precipitate was spread as uniformly as possible, with the aid of a glass rod and a little alcohol, over a flat polished brass plate, about 7 cm. in diameter. When the alcohol had evaporated, the less firmly adhering particles were brushed off, care being taken to guard the edges and back of the plate from radioactive contamination. The films so prepared were so thin

[1] Compare the work of McCoy and Viol, *loc. cit.*, on the separation of Th *B*, *C*, and *D* from Th *X*.

as to be almost invisible; the differential absorption of α-rays in such films was therefore negligibly small.

The time of precipitation of the sulphate was taken as zero time, as at this moment the precipitate was free from all of the subsequent products of radium. That the foregoing method completely freed the radium from all of its active products was shown both by control experiments and by the fact that the activity increased at a regular rate from the start. About thirty minutes elapsed between the time when the sulphates were precipitated and the time of making the first measurements. The activity measurements were made in a gold-leaf electroscope, as previously described,[1] the active films being placed 7 cm. below the charged electrode, thus allowing all rays to reach their full ranges. Sufficient potential (about 600 volts) was used to insure practically complete saturation currents for the weak ionization produced. All activities were measured in comparison with a standard film of uranium oxide, the activities given being in terms of this standard. All measurements were made with the greatest care, and corrections were made for the accurately determined natural leak, which in every case was less than 1 per cent of the standard. The initial activity of each film was less than, the final activity greater than, the standard. The activity increased nearly linearly for the first six hours, so that by a small extrapolation the activity at time zero could be determined with a high degree of accuracy. The activities in terms of the standard are given in Table II for two films.

TABLE II

THE INITIAL AND FINAL ACTIVITIES OF RADIUM (UNCORRECTED)

Film	Initial Activity	Final Activity 8	Ratio Uncorrected
1.....	0.858	4.325	5.043
2.....	0.558	2.832	5.075

But these results are subject to three corrections, viz.: the activity due to the β-rays, the escape of emanation from the film either by diffusion or by recoil, and the loss of other products by recoil.

The activity due to β-rays was determined by placing consecutive layers of aluminium foil over the Ra-$BaSO_4$ film, the first layer being of sufficient thickness to absorb all α-rays and measuring the activity with each additional layer in the same electroscope as was used for the

[1] McCoy and Ashman, *Am. Jour. Sci.*, **26**, 521, 1908.

α-ray measurements. By plotting the activities against the thickness of covering, and extrapolating to the axis of the activities, the β-ray activity could be ascertained with a fair degree of accuracy. This activity must be subtracted from the final activity of the film.

Since Kolowrat[1] has shown that the β-ray activity of radium free from its products is only 2 per cent of the β-ray activity of radium in equilibrium with its short-lived products, and since the β-ray activity of the latter as measured in the electroscope used in this work was only about 0.5 per cent of the α-ray activity, it follows that it is not necessary to apply any correction for β-ray activity of the radium itself.

The amount of emanation lost by the film was determined by the use of a circular brass box, as shown in Fig. 1. The cover *A*, fitted with two small bore tubes *E* and *G*, was ground so as to fit very tightly over the lower compartment *B*. In the lower compartment was a recess about 0.2 cm. in depth and 8 cm. in diameter. Small-bore glass tubes drawn out at one end, *C* and *D*, were attached to the tubes *E* and *G* by means of short pieces of thick-walled rubber tubing. The Ra-$BaSO_4$ film was placed in *B*, the cover *A* fitted on, and all joints sealed with wax. The ends of *C* and *D* were then sealed by fusion. After an interval of 40 days or more the emanation which had accumulated was drawn into an emanation electroscope by a stream of air, care being taken to prevent any loss of the accumulated emanation and also to prevent any appreciable diminution of pressure within the box which might withdraw some of the Em from the film. The rate of discharge of the electroscope was measured after the emanation had stood in it for three hours.

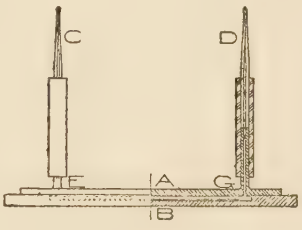

Fig. 1

In order to find what fraction this quantity of Em was of the equilibrium quantity in the Ra-$BaSO_4$ film, two additional determinations were necessary. One c.c. of the original radium solution was diluted and then freed from subsequent active products, as described in a preceding paragraph. By means of a small weight-pipette, an accurately weighed portion of this solution was taken and uniformly distributed over the surface of a flat platinum plate and evaporated to dryness. The activity of the residue, which was entirely invisible, was measured within twenty minutes, and the measurements extended over a short interval in order

[1] *Le Radium*, **7**, 269, 1910.

to be able to get the initial activity by extrapolation. To find the activity of the emanation from this quantity of radium, a known portion of the solution in the weight-pipette was run into a small round-bottom flask containing about 10 c.c. of dilute hydrochloric acid. The flask was well stopped with a two-hole rubber stopper fitted with delivering tubes, one of which extended into the solution. A current of air was bubbled through the solution for 30 minutes to drive off the accumulated emanation, and the flask was then sealed by fusing the ends of the delivery tubes. After an interval of a few days the emanation was drawn into the emanation electroscope by allowing air to bubble through the solution, which was heated near its boiling-point. After three hours the rate of discharge of the electroscope was measured.

The corrections for loss of emanation by the film were made as follows:

Initial activity of film No. 1	0.858
Initial activity of Ra on the platinum plate	.660

The radium on the platinum plate was obtained from 1.4942 gm. of solution. After 3 days 21.5 hours 1.5738 gm. of the same solution gave a quantity of Em which discharged the electroscope in 46.45 seconds. Since for 3 days 21.5 hours, $1-e^{-\lambda t}=0.5036$, the equilibrium amount of Em from the solution would have discharged the electroscope in $0.5036\times 46.45=23.40$ seconds. Therefore the equilibrium amount of Em from 1.4942 gm. of this solution would discharge the electroscope in 24.64 seconds. That is, a radium film, free from all subsequent products of radium, having an initial α-ray activity of 0.660, produces an equilibrium quantity of emanation which discharges the emanation electroscope in 24.64 seconds. It then follows that the equilibrium quantity of emanation from film No. 1, which has an initial activity of 0.858, would discharge the emanation electroscope in 18.97 seconds. The emanation which had escaped from film No. 1, when the latter had been sealed up 40 days or more, discharged the emanation electroscope in 1,748 seconds; therefore 1.08 per cent of the equilibrium quantity of Em escaped from the film. This means that the quantity of emanation and the short-lived products in the film is 1.08 per cent too low. In this film the activity of the subsequent products of Ra is $4.297-0.858=3.439$, which value is 1.08 per cent too low. Hence the true activity of the products, if no Em had escaped, would be 3.476.

To find the loss of activity due to recoil, a polished brass plate 7 cm. in diameter was placed 1 mm. above, and completely insulated from, film No. 1. A potential of 110 volts was maintained for six weeks, the

upper plate being kept negatively charged. The activity of the plate was measured as quickly as possible after removing the potential, four minutes elapsing from the time the potential was removed to the mean time of making the measurements. The activity of the active matter which collected on the plate was 0.0374. Assuming that the active matter on the plate at the instant the potential was removed was Ra*A*, Ra*B*, and Ra*C* in equilibrium, the activity of the matter on this plate four minutes after the potential is removed is approximately 70 per cent of its initial value.[1] Therefore the initial activity of the matter on the plate was 0.0534. To find what quantity of the matter on the plate is due to active deposit from escaped emanation and what quantity is due to

TABLE III

THE INITIAL AND FINAL ACTIVITIES OF RA (CORRECTED)

Film	Initial Activity I_0	Final Activity I_0	I_0/I
1	0.858	4.363	5.085
2	0.558	2.863	5.133
Mean			5.109

direct recoil, it is necessary to recall that the emanation lost by this film was 1.08 per cent of the equilibrium quantity, or the activity of the products Em, Ra*A*, and Ra*C* lost was 0.037. Assuming that the activities are proportional to the two-thirds powers of the ranges, the fraction of the activity due to Ra*A*+Ra*C* is 65 per cent of the total activity due to Em+Ra*A*+Ra*C*, or 0.0241, and that due to recoil is 0.0534−0.0241=0.0293.[2]

Table III gives the results of two determinations. The final activity is corrected for β-ray activity, loss of emanation, and loss by recoil, these corrections being determined separately for each film.

[1] Rutherford, *Radioactive Substances and Their Radiations* (1913), p. 491.

[2] It must be pointed out that this value is calculated on the assumption that at the instant the potential is removed the active matter on the plate is Ra*A*+Ra*B*+Ra*C* in equilibrium, and there is a decided drop in activity before the first measurement is made, due to the rapid decay of Ra*A*. In the case of the active matter due to active deposit we do have this equilibrium, but in the case of recoil atoms there is in all probability an excess of Ra*C* atoms over the equilibrium number of Ra*A* atoms. This would mean that the percentage of the activity which decayed during the interval between the time the potential was removed and the time of measurement would not be so great as that calculated upon complete equilibrium, and the value of the loss by recoil would be even less than that calculated above. However, the loss by recoil is so small that the value calculated above is certainly correct within experimental error, and it represents the maximum value.

In the series Ra—Em—RaA—RaC it is very probable that each member when present in equilibrium amount produces the same number of α-particles per unit time; if this is so, the equation

$$I = kR^{\frac{3}{2}}$$

leads to the theoretical results shown in Table IV.

TABLE IV

	Ranges at 15°	$R^{\frac{3}{2}}$	Relative Activities	
			Calculated	Found
Ra	3.30	2.217	1.00	(1.00)
Em	4.16	2.586	1.17	
RaA	4.75	2.826	1.28 } 4.09	4.11
RaC	6.94	3.639	1.64	

The only previous determination of the relative activities of radium and its products was made by Boltwood.[1] In these experiments the films were made by the evaporation of a chloride solution. Since such films gave off very large fractions of the emanation produced (in one case as high as 65 per cent), it is not surprising that the results obtained were not very accurate. Instead of a ratio of 4.11 given here (last column, Table IV), Boltwood found 4.65. For several years this result was looked upon as satisfactory,[2] since it was in good agreement with that calculated upon the assumption that the number of ions produced by an α-particle is proportional to the first power of its range[3] instead of the two-thirds power.

The good agreement of this result with the theoretical value as calculated by the equation $I = kR^{\frac{3}{2}}$, the correctness of which may be considered as already established, shows that only those members which are here considered play significant parts in the α-ray activity of the radium series, and that the accepted ranges are at least approximately correct.

[1] *Phys. Zeit.*, **7**, 489, 1906; *Le Radium*, **3**, 170, 1906.

[2] Rutherford, *Radioactive Substances* (1913), p. 447.

[3] Boltwood, *loc. cit.*

CHAPTER II

THE RELATION BETWEEN α-RAY ACTIVITIES AND RANGES OF RADIOACTINIUM AND ITS SUBSEQUENT PRODUCTS

A study of the actinium series was made along the same lines as in the preceding part of this paper, and radioactinium, free from actinium itself as well as actinium *X* and subsequent products, was prepared, thin films made, and the α-ray activities measured from time to time. The activities, of course, increase to a certain interval, then decrease, owing to the formation of actinium *X* and its products and the consequent decay of the whole.

Table V gives the latest available data for this series.

TABLE V

THE ACTINIUM SERIES

	Symbols	Periods	Rays	Ranges (Centimeters)
Actinium	Ac	?	.....	.....
Radioactinium	Rn	18.88 days*	α, β	4.40†
Actinium *X*	Ac*X*	11.35 days*	α	4.40
Emanation	Em	3.9 seconds	α	5.70
Actinium *A*	*A*	0.002 seconds	α	6.50
Actinium *B*	*B*	36 minutes	β	.....
Actinium *C*	*C*	2.1 minutes	α	5.40
Actinium *D*	*D*	4.71 minutes	β, γ	.....

* This paper. The previously accepted periods of radioactinium and actinium *X* were 19.5 days and 10.2 days respectively.

† The range of radioactinium found by Geiger was 4.60 cm.; the value given above is that given in this paper.

If f_1 is the fraction of the original Rn left after an interval of t days and f_2 is the fraction for Ac*X*, unit amount being the equilibrium quantity corresponding to the initial amount of Rn, then the activity A, at time t, resulting from unit initial quantity of Rn, is given by the equation:

$$A = f_1 + f_2 x \qquad (1)$$

where x is the α-ray activity of the equilibrium quantity of Ac*X* plus products for unit quantity of Rn. Strictly speaking, for intervals of less than 3 or 4 days one should take into account the fact that the products

of Ac*X* are not in equilibrium with the latter; practically, however, for longer intervals the simple equation (1) is entirely sufficient. If λ_1 and λ_2 are the decay constants of Rn and Ac*X*, respectively, then

$$f_1 = e^{-\lambda_1 t}$$

and

$$f_2 = \frac{\lambda_2}{\lambda_2 - \lambda_1}(e^{-\lambda_1 t} - e^{-\lambda_2 t}).$$

The periods being 18.8 days and 11.35 days, respectively, $\lambda_1 = 0.0369$ and $\lambda_2 = 0.0611$.

The actinium used in this work had been found to be free from all but negligible traces of radium and thorium and their active products, emanation tests proving the absence of radium and active deposit experiments proving that of thorium. It contained, however, an appreciable amount of ionium. To the solution of the actinium-bearing material in dilute hydrochloric acid a few milligrams of thorium nitrate was added and the latter then precipitated with hydrogen peroxide. The filtrate contained all the actinium and was apparently free from Rn and Io; but, to be certain that no trace of the latter remained in the Ac, the treatment with Th and hydrogen peroxide was repeated three times. To the purified actinium solution 1 c.c. of 5 per cent aluminium chloride solution was added and ammonia gas (free from carbon dioxide) passed in. The aluminium hydroxide was filtered out, dissolved in hydrochloric acid, and precipitated with ammonia once more. The filtrate from the first aluminium precipitate contained two-thirds of the Ac*X*; that from the second the larger part of the balance; while 6 per cent of the Ac*X* remained in the third aluminium precipitate, which contained practically all of the Ac. The precipitations with ammonia had freed the Ac from the minute amount of mesothorium introduced with the few milligrams of Th used. This Ac solution stood for several months, during which time a large amount of Rn formed. The Rn was then separated from this solution, which had a volume of 5 c.c. by adding 3 drops of a 2 per cent solution of thorium nitrate, which had just been freed from mesothorium, and precipitating the Th by hydrogen peroxide. The precipitate was filtered out, dissolved in dilute hydrochloric acid and potassium iodide, and reprecipitated by hydrogen peroxide four times more. The 10 c.c. of acid solution of the last Th precipitate which contained all the Rn, but was entirely free from Ac*X* and its products, was treated with oxalic acid. The precipitate of 3 or 4 mg. of thorium

oxalate contained all of the Rn. It was separated from the solution by a centrifuge and washed thoroughly with water and then with alcohol. A small portion was then spread on a metal plate in an exceedingly thin film, the activity measurements of which are given in Table VI. In this table x is the activity of AcX+Em+A+B+C+D in terms of the activity of the equilibrium amount of Rn as unity.

TABLE VI

THE α-RAY ACTIVITY CURVE OF RADIOACTINIUM INITIALLY FREE FROM ITS PRODUCTS. FILM NO. 4

Interval in Days	Activity	x
0.000	1.000	
5.101	1.933	4.54
6.025	2.045	4.53
15.76	2.597	4.55
16.08	2.620	4.59
17.07	2.623	4.59
17.80	2.629	4.60
20.05	2.593	4.56
23.10	2.527	4.54
27.09	2.397	4.54
31.10	2.281	4.63
36.04	2.053	4.60
39.97	1.881	4.61
206.0	0.007	
Mean		4.573

The activity at the end of 206 days (Table VI) was found to be 0.007; of this, 0.001 was calculated to be due to remaining Rn and products; the balance, 0.006, represents the constant activity of the minute amount of thorium present. The activities given in Table VI have been corrected for this constant thorium activity. The activity measurements were made in the α-ray electroscope previously described.[1] The active films were placed 6.5 cm. below the charged electrode, thus allowing all rays to reach their full ranges. The activities of the films varied between one-half and one and one-half that of the standard film of uranium oxide. Sufficient potential, 500 to 600 volts, was used to insure practically complete saturation currents for the weak ionization measured.

Three other series of measurements like those represented by Table II were made with films made from two additional lots of radioactinium,

[1] McCoy and Ashman, *loc. cit.*

each prepared and purified separately. The results for the four films are summarized in Table VII.

The value of x thus found is subject to a correction, which was estimated to be 2.5 per cent, due to the effects of β-rays, recoil, and loss of emanation. The corrected value is 4.68. By direct measurement it was found that the β-rays, largely from actinium D, increased the value of x, 0.5 per cent for the α-ray electroscope used in our measurements. To find the loss of activity due to recoil and loss of emanation a brass plate charged to a negative potential of 110 volts was placed 1 mm. above the radioactive film in a closed vessel, and the activity which deposited on the plate during the first 16 days following the preparation of the radioactinium film was measured. Almost exactly half of the activity of the deposit was due to AcC; the balance decayed with the period of AcX, the presence of the latter substance being due to

TABLE VII

No. of Film	No. of Observations	x
1	18	4.59
2	14	4.57
3	15	4.55
4	12	4.57
Mean		4.57

recoil. Assuming that all of the AcC lost by the film was deposited on the plate, the correction to x on this account would amount to 2 per cent. The correction to AcX, which is accompanied of course by Em and A, is also apparently 2 per cent, but should be taken somewhat less by reason of the probable extensive escape in the ionization chamber of the Em and A from the surface of the brass plate into the space above, where they would cause greater ionization than if they remained wholly on the plate. The true correction, however, was taken to be 1.8 per cent instead of 2 per cent. A further correction should be made because of the volatilization of Em and therefore of A from the principal film in the ionization chamber of the electroscope. From the amount of C in the active deposit, we estimate that 2 per cent of the whole Em is present in gaseous form in the electroscope, and that this would cause the value of x as found to be 0.8 per cent too high. The combined effect of these corrections is $2+1.8-0.5-0.8=2.5$ per cent. Taking x uncorrected as 4.57, the corrected value becomes 4.68.

Table VIII shows the ranges, R, at 15° and 76 cm., $R^{\frac{2}{3}}$, and the percentage activity of each α-ray member of the series; these percentages are taken proportional to the corresponding values of $R^{\frac{2}{3}}$, it being assumed that the equilibrium amount of each member of the series produces the same number of α-particles per second.[1] The values given in the last column of Table VIII are those found by experiment: for radioactinium the "activity found" is $1/(1+x)=17.6$ per cent of the whole.

TABLE VIII

	Ranges at 15°	$R^{\frac{2}{3}}$	Percentage Activity	
			Calculated	Found
Radioactinium	4.40	2.69	17.8	17.6
Actinium *X*	4.40	2.69	17.8	
Emanation	5.70	3.19	21.1	82.4
Actinium *A*	6.50	3.49	23.0 (82.2)	
Actinium *C*	5.40	3.08	20.3	
			100.0	

The value of $\Sigma R^{\frac{2}{3}}$ for Ac*X*+Em+*A*+*C* divided by $R^{\frac{2}{3}}$ for Rn gives 4.62, which is therefore the theoretical value of x. The close agreement of this result with that found by experiment, 4.68, is further evidence, if such were necessary, that the roll of the α-ray members of the actinium series is now complete and that the constants given in Tables V and VIII may be accepted with considerable confidence as being at least close approximates to the true values.

[1] While it is probable that Ac*C* is complex, the number of α-particles of longer range than 5.4 cm. compared with those of this range is so small—0.15 per cent—that we need not take them into account here. See Marsden and Perkins, *Phil. Mag.*, **27**, 700, 1914.

CHAPTER III

NOTES

NOTE 1. THE PERIOD OF RADIOACTINIUM

Hahn's early work[1] on radioactinium indicated a period of 19.5 days. This value has been accepted during the past eight years and was thought to be confirmed by Rothenbach,[2] working under the direction of Professor Hahn. In determining the period of a radioactive substance, which produces products of considerably shorter life, it is usually practicable to consider that the rate of decay is exponential after a sufficient lapse of time. It was by this method of calculation that the period of radioactinium was determined by Hahn and by Rothenbach. However, in case the period of one or more of the products is the same order of magnitude as that of the mother-substance, this simple treatment of the problem is not accurate, and it becomes necessary to make the following modification:

The familiar equation which has been previously used in the form

$$f_2=\frac{\lambda_2}{\lambda_2-\lambda_1}(e^{-\lambda_1 t}-e^{-\lambda_2 t})$$

may be written

$$f_2=\frac{\lambda_2}{\lambda_2-\lambda_1}f_1[1-e^{-(\lambda_2-\lambda_1)t}]=\frac{p\lambda_2}{\lambda_2-\lambda_1},$$

if for $1-e^{-(\lambda_2-\lambda_1)t}$ we write p. The equation

$$A=f_1+f_2x$$

then becomes

$$A=f_1\left[1+\frac{p\lambda_2 x}{\lambda_2-\lambda_1}\right].$$

Now the limiting value of f_2 is given by

$$f_2=\frac{\lambda_2}{\lambda_2-\lambda_1}f_1,$$

[1] *Phil. Mag.*, **12**, 244, 1906; **13**, 165, 1907.

[2] Dissertation (Berlin, 1913).

and to calculate the period of Rn by the simple exponential equation is to assume that f_2 has approached this limitating value sufficiently closely. But this is by no means the case, even after a much longer time than that over which Hahn's and Rothenbach's observations were carried. After 115 days the activity of a Rn film is about 6 per cent less than it would be if the limiting ratio of AcX were present. Let us represent by A' the activity of the film if this limiting ratio of AcX (+ products) were present: then

$$A' = f_1\left[1+\frac{\lambda_2 x}{\lambda_2-\lambda_1}\right]$$

and

$$\frac{A'}{A} = \frac{\lambda_2-\lambda_1+\lambda_2 x}{\lambda_2-\lambda_1+p\lambda_2 x} = q,$$

or we may write

$$A' = Aq.$$

In order to find the period of Rn, films were made as previously described, and very careful measurements were made of their initial activity, extrapolating from the first measurements made 45 minutes after the precipitation of the Rn with the thorium oxalate to find the true activity at time zero, which value was used in check calculations. These films were allowed to decay a suitable length of time, and a series of measurements was made on each at convenient intervals. The films were then allowed to stand for nearly a year, and the activities again measured over a short period. This activity, which was in each case nearly constant, was due to the small amount of thorium present, all Rn having decayed. All measurements on each film were then respectively corrected.

Table IX gives the results of a series of measurements made on one of the films, calculated on the basis that $x=4.68$.

Three other series of measurements of different films gave the results found in Table X. The low result, 18.75 days, for the last series was caused by three very low values, found on successive measurements on the ninth, twelfth, and fourteenth days, viz., 18.56, 18.57, and 18.67. On both the fifteenth and sixteenth days, however, the measurements gave 18.84 days, and it is probable that these low results were caused by some undiscovered error in the activity measurements. If these low results are omitted from the mean, the figure for this series becomes

18.87 days, a value in good agreement with the means of the other three series.

Further check calculations were made of the activities at various times upon the assumption that the period of Rn is 19.0 and 19.1 days. If the period of Rn is 19.1 days, the mean difference between the activities found and calculated is 5.9 per cent; for a period of 19.0 days the difference is 3.7 per cent, while for a period of 18.8 days the difference is only 0.8 per cent. It is therefore perfectly clear that the old value, 19.5 days, is far from the true value and can no longer be supported.

TABLE IX

Age of Film in Days	Interval since 92.21 Day	Activity Corrected A	q	A'	Period
91.21.....	0.0	1.658	1.110	1.840	.....
100.97.....	8.76	1.227	1.087	1.334	18.86
103.98.....	11.77	1.106	1.080	1.195	18.88
108.20.....	15.99	.952	1.072	1.021	18.81
112.92.....	20.71	.809	1.064	.861	18.89
117.89.....	25.68	.678	1.056	.717	18.88
119.16.....	26.95	.652	1.054	.687	18.97
Mean.....	.....	.....	.....	.....	18.88

TABLE X

Age of Film at First Measurement	Age of Film at Last Measurement	Number of Measurements	Period
60.1 days	109.2 days	11	18.88
60.1 days	118.0 days	12	18.88
104.0 days	120.0 days	7	18.75

The difference between the value 18.8 for the period of radioactinium and that of Hahn and Rothenbach is wholly due to the fact that in the latter case the formula used in the calculation was not sufficiently accurate. The experimental results given here are in satisfactory agreement with theirs and indicate also a period of 19.5 days if the calculation is made by the simple exponential equation used by Hahn and Rothenbach. The latter's calculations were based on measurements made between the one hundred and fifteenth and one hundred and seventy-fourth day. Now a simple calculation will show that, if the period as found by the simple exponential equation is 19.5 days for the interval between 120 and 139.5 days, then by use of the correct formula used here the same data show the true period to be 18.89 days.

These measurements indicate that the period of radioactinium is a little higher than 18.8 days, which value was used in finding the value $x=4.68$. If, as is very probable, the period is 18.88 days, the previous experimental results give $x=4.67$; the difference is not great, and the lower value of x is in even closer agreement with the value calculated from the ranges, viz., 4.63.

NOTE 2. DETERMINATION OF THE RANGE OF RADIOACTINIUM

From the value found for the activity of the products of radioactinium compared with radioactinium itself it was suspected that either the accepted range of radioactinium was too great or that of Ac*X* was too small. The values found by Geiger[1] for Rn and Ac*X* at 15° and 760 mm. were 4.60 and 4.40 cm., respectively. Furthermore, by Geiger's law relating ranges and decay constants, the range of Rn should be less than that of Ac*X*. As it was a comparatively easy task to determine the range of Rn, this measurement was carried out with the use of a modification of Geiger's spherical flask apparatus. The flask, which was chosen from a large stock, was almost perfectly spherical, except in the region near the neck. Its internal radius was 6.7 cm.

The radiothorium was prepared by the same method as that used in preparing this substance for the activity measurements. A large quantity of actinium was used, and but one drop of a 0.4 per cent thorium nitrate solution, $=0.1$ mg., ThO_2. The thorium was precipitated three times with hydrogen peroxide and was converted into oxalate, which was separated by means of a centrifuge and washed with dilute hydrochloric acid and finally with alcohol. A small portion of this oxalate was made into a very thin film, about 1 mm. in diameter on the center of the brass disk of the range apparatus. The range measurements were completed within two or three hours from the time of the oxalate precipitation; from this it follows that the maximum amount of Ac*X* formed did not exceed 0.25 per cent of the equilibrium amount. The temperature was read at frequent intervals during the measurement and always remained constant within one degree.

The results of one determination are shown graphically in Fig. 2, which is drawn to scale. The break comes at 504 mm. of mercury, and as the temperature was 20°, this gives as the range of radioactinium 4.17 cm. at 760 mm. and 0°, or 4.40 cm., at 15°. Two other determinations were made, each with separately prepared samples of radioactinium.

[1] *Phil. Mag.*, **24**, 653, 1912.

One gave 4.38 cm., the other 4.43 cm., at 15°; the mean of the three results is 4.40 cm. for 15°. This is 0.20 cm. lower than Geiger found for radioactinium and is identical with Geiger's value of actinium *X*. The periods of radioactinium and actinium *X* are 18.8 and 11.35 days, respectively, and if the range of the former is 4.40 cm. that of the latter

Fig. 2

should by Geiger's law be 4.45 cm., which differs from the value found by Geiger by scarcely more than the experimental error of the measurements.

NOTE 3. THE PERIOD OF ACTINIUM *X*

Kolowrat[1] gives in his annual tables of radioactive constants the value for the period of actinium *X* as 10 to 11 days. Goldewski[2] has previously reported this figure to be 10.2 days. Hahn and Rothenbach[3] have recently given the value to be 11.6±0.1 days. In view of the uncertainty of this figure, work along this line was undertaken to ascertain its true value.

[1] *Le Radium, loc. cit.*

[2] *Phil. Mag.*, 10, 35, 1905.

[3] *Phys. Zeit.*, 14, 409, 1913.

Radioactinium free from actinium itself and all subsequent products was prepared as previously described, except that the precipitation of the thorium as oxalate was omitted. The solution was allowed to stand for about two weeks; a portion of this solution was then nearly neutralized with ammonia and the thorium precipitated by means of hydrogen peroxide. The solution which contained the actinium *X* was filtered and 10 drops of 2 per cent thorium nitrate solution were added. ThO_2 was again precipitated and the solution filtered. This treatment was repeated three more times, insuring the complete removal of Rn. A portion of the last filtrate was placed in a 15 c.c. centrifuged tube, 1 c.c. of 0.01 *N* $BaCl_2$ added, then a few drops of dilute H_2SO_4. The solution was allowed to stand 15 minutes and then centrifuged. The $BaSO_4$ which carried

TABLE XI

Time in Days	Activity	Decay Constant	Time in Days	Activity	Decay Constant
0.00.....	1.000	.....	0.00.....	1.000	.....
3.06.....	0.830	0.0610	3.71.....	0.798	0.0609
5.04.....	0.736	0.0610	4.71.....	0.751	0.0609
6.77.....	0.659	0.0616	6.72.....	0.664	0.0610
9.83.....	0.546	0.0616	8.84.....	0.581	0.0614
11.99.....	0.480	0.0613	9.72.....	0.551	0.0613
12.72.....	0.458	0.0614	12.81.....	0.457	0.0611
15.92.....	0.380	0.0610	17.00.....	0.357	0.0607
19.08.....	0.318	0.0608			
Mean.....	.....	0.0612	Mean.....	.....	0.0610

down the actinium *X* was then washed and made into films as previously described in making the Ra'$BaSO_4$ films. Two films were prepared in this manner. Each was allowed to stand for two days before the series of measurements was begun. The measurements were made in the α-ray electroscope used in the previous work, the active films being placed 7 cm. below the charged electrode. All activities were measured in comparison with a standard film of uranium oxide, and corrections were made in every case for the natural leak. A small correction was applied for the presence of thorium *X*, introduced by the thorium nitrate solution. This correction was obtained by running a blank experiment, and in every case it was less than 0.3 per cent of the total activity.

Table XI gives the values obtained, the activities given being corrected for all known factors.

The mean of the values for the decayed constants is therefore 0.0611 day^{-1}, corresponding to a period of 11.35 days. This value is in close agreement with that of Hahn and Rothenback and disproves that given by Godlewski.

In conclusion the author wishes to express his most sincere thanks to Professor Herbert N. McCoy, whose interest, co-operation, and encouragement have made the completion of this work possible.